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On the assignment of vibration frequencies of ortho-, meta- and para-cresols

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The assignment of vibration frequencies of three isomeric cresols in the region 200–700 cm^{-1} has been made. Some of the inconsistencies in the vibrational assignments of the frequencies between 700–1680 cm^{-1} for all the three molecules made by previous workers have been pointed out and suitable alternative assignments for them have been proposed.

Introduction

The Raman spectra of ortho-, meta- and para-cresols in the liquid state have been investigated by several workers (Kohlrausch & Pongratz 1933, Magat 1936, Biswas 1955) and a partial assignment of the Raman frequencies is given in the literature (Mecke-Kerkhof 1951) Later, the infrared absorption spectra of para-cresol and a large number of para-di-substituted benzene compounds in the frequency interval 650 cm^{-1}–1650 cm^{-1} were studied by Garrigou-Lagrange *et al.* (1958), who also made assignments of the observed vibration frequencies. Recently, similar investigations in the case of ortho- and meta- disubstituted benzenes including ortho- and meta-cresols have been carried out respectively by Brigodiot & Lebas (1965) and by Garrigou-Lagrange *et al* (1966). In view of the facts that some of the vibrational assignments of para-cresol proposed by Garrigou-Lagrange *et al.* (1958) are inconsistent with the states of polarisation of the Raman lines and strengths of the infrared absorption bands corresponding to the proposed modes of vibration and that assignments of vibrational frequencies below 500 cm^{-1} for all the three isomers and especially for ortho-cresol have not been made earlier, it was thought worthwhile to attempt complete assignments of all the vibration frequencies of the three isomeric molecules observed in Raman scattering and in infrared absorption. For this purpose the Raman spectra of the three compounds in liquid state and the infrared absorption spectra of the pure liquids and their solutions in suitable solvents have been reinvestigated. A discussion of the results obtained is presented in this paper.

Experimental

Chemically pure samples of ortho-,meta- and para-cresols obtained from E. Merck (Germany) were subjected to fractional distillation and the proper fractions were distilled under reduced pressure. The distilled liquids were

dehydrated before use. Guaranteed reagent quality carbon tetrochloride and chloroform were properly dehydrated and used as solvents for infrared absorption studies The Raman spectra of the pure liquids, the states of polarisation of the Raman lines, and the infrared absorption spectra of the pure compounds in the liquid state and in solutions were studied by methods described earlier (Chattopadhyay & Jha, 1968). All the Raman spectra were recorded on a Fuess glass spectrograph having a dispersion of 13 Å/mm and 19Å/mm in the Hg 4047Å and 4358Å regions, respectively, while the infrared absorption spectra were studied on a Perkin Elmer Model 21 double beam spectrophotometer provided with rocksalt optics.

Results

The Raman frequency shifts ($\Delta\nu$ cm^{-1}) their relative intensities and states of polarisation for all the three liquids together with the positions of the infrared absorption bands (ν cm^{-1}) and their relative strengths in the case of the pure liquids and their solutions are given in tables 1, 2 and 3. For any compound the Raman shifts recorded in the table are the averages of all the data available in the literature and those obtained in the present investigation. For comparison the data of the infrared absorption bands reported by previous workers have also been included in the tables. The tables contain the assignments of the vibration frequencies proposed by the present authors together with those given by previous investigators. Since many of the vibrational assignments made by previous workers do not require any modification the assignment of only those vibration frequencies for which no assignment has been made by previous workers is discussed in the following paragraph Moreover, the inconsistencies in the assignment of some of the frequencies of vibration published in the literature are pointed out and suitable assignments for them have been suggested. Unless otherwise stated, the mode numbers of benzene mentioned in the text and in the tables are those due to Pitzer & Scott (1943).

a) Para-cresol

From table 1, it is seen that for the molecule of para-cresol there are six vibration frequencies below 650 cm^{-1} which have not been assigned by Garrigou-Lagrange *et al.* (1958). However, the frequencies 465 cm^{-1} and 644 cm^{-1} have been assigned by Mecke-Kerkhof (1951), to modes 6A and 6B respectively, of benzene with which the present authors are in agreement. The very weak Raman line 406 cm^{-1} observed by Biswas (1955) certainly corresponds to mode 16*A* of benzene, while the weak broad Raman line 282 cm^{-1} (Biswas, 1955) may arise from the modes 16*B* and 18*B* of benzene This assignment has been made on the basis of a calculation of the vibrational frequencies of para-xylene and some other para-dihalobenzenes by Schmidt *et al* (1960) Following the same authors the medium intensity broad and depolarised Raman line 338 cm^{-1} has been assigned to the modes 9*B* and 10*B*. According to Mecke-Kerkhof (1951) this line originates

from a mode involving in-plane bending motions of the substituents very similar to that in mode 15 of Stojiljkovic & Whiffen (1958) though contribution from mode 10 due to the same authors cannot be entirely ruled out. The weak Raman line 510 cm^{-1} in accordance with the calculation of Schmidt *et al.* (1960) has been assigned to mode 11 of benzene.

Garrigou-Lagrange *et al* (1958) have assigned the medium intensity polarised Raman line 824 cm^{-1} having its counterpart in the strong infrared band at 826 cm^{-1} to mode 10*A* of benzene. This mode in C_{2v} symmetry is inactive in the infrared absorption and also being an out of plane vibration cannot give rise to a polarised Raman line Therefore, the weak Raman line at 809 cm^{-1} (Garrigou-Lagrange *et al* 1958) has been assigned to this mode of vibration. The frequency 824 cm^{-1} is believed to correspond to mode 12 of benzene and following Sirkar & Bishui (1968) the strong polarised Raman line at 844 cm^{-1} is assigned to mode 1 of benzene.

The weak Raman line at 969 cm^{-1}, for which no corresponding infrared band has been observed, is assigned to mode 17*A* of benzene. This is in keeping with the infrared inactive nature of this mode in C_{2v} symmetry though according to the calculation of Schmidt *et al* (1960) this line might also have originated from mode 5 of benzene. From the above considerations the assignment of the infrared bands at 922 cm^{-1} and 985 cm^{-1}, to modes 5 and 17*A* respectively, of benzene by Garrigou-Lagrange *et al* (1958) does not seem satisfactory.

The two polarised Raman lines of medium intensity at 1216 cm^{-1} and 1255cm^{-1} have been assigned by Garrigou-Lagrange *et al.* (1958) to modes *e* and *e'* of Kohlrausch All para-substituted toluenes show a Raman line with a frequency shift of about 1210 cm^{-1} while in all para-substituted phenols a Raman line at about 1255 cm^{-1} is observed. So it may be concluded that in the case of para-cresol the line 1216 cm^{-1} originates from a mode of vibration involving the motion of the methyl group and the other line 1253 cm^{-1} is due to a mode which involves the motion of the hydroxyl group. Moreover, in the present case there is no infrared absorption band corresponding to the line 1216 cm^{-1} while a strong infrared band 1258 cm^{-1} corresponding to the Raman line 1253 cm^{-1} has been observed. These facts indicate that in the mode of vibration giving rise to the former line, the displacements of the nulei are symmetrical but in the latter case some asymmetry in the displacements occurs. It is suggested that these two lines originate from modes of vibration similar to the mode *q* proposed by Randle & Whiffen (1955) in the case of mono-substituted benzenes. In one of these modes the trigonal displacements of 1, 3, 5 carbon atoms are coupled with the stretching of C-CH_3 bond and in the other similar coupling takes place between the stretching of the C-OH bond and the trigonal mode involving 2, 4, 6 carbon atoms. These are designated by the symbols *q* and *q'*, respectively.

Garrigou-Lagrange *et al.* (1958) have assigned the infrared band at 1430 cm^{-1} to mode 14 of benzene. Though this is in accordance with the infrared active

nature of the mode in benzene the frequency is somewhat higher than that of benzene. Moreover, it may be noted that in the case of the two other cresols there are weak Raman lines at 1440 cm^{-1} which are most conveniently assigned to asymmetric CH bending mode of the methyl group in these molecules. Accordingly, the infrared band 1434 cm^{-1} has been assigned to asymmetric CH bending mode in the methyl group and the strong infrared band at 1360 cm^{-1} due to the pure liquid has been assigned to mode 14 of benzene.

In the Raman spectrum of para-cresol, as in the case of two other cresols, a medium intensity polarised Raman line at 2889 cm^{-1} has been observed. This has been assigned to symmetric C-H stretching vibration in the methyl group of the molecule. The assignments of asymmetric CH stretching vibrations and other C-H stretching vibrations of the phenyl ring are shown in table 1.

(b) Meta-cresol

The Raman spectrum of meta-cresol shows four Raman lines with frequency shifts below 400 cm^{-1} (table 2) for which no assignment has been made by Garrigou-Lagrange *et al* (1966). In proposing assignment of these lines we have been guided by the calculations of Bogomolov (1962) in the case of meta-xylene and those of Nonnenmacher & Mecke (1961) for meta-derivatives of benzene including meta-xylene and resorcinol These calculations show that the frequency of both the modes 11 and 10*A* of benzene are reduced and that the frequency of the latter mode is slightly higher than that of the former. Accordingly, the frequencies 214 and 241 cm^{-1} have been assigned to mode 11 and 10*A*, respectively. Moreover, Bogomolov (1962) has shown that in the case of meta-xylene the frequencies of mode 9*A* and 15 of benzene are considerably lowered, but they are higher than those corresponding to the modes 11 and 10*A*. With these considerations the depolarised Raman lines at 304 cm^{-1} and 565 cm^{-1} are assigned to modes 9*A* and 15, respectively.

Garrigou-Lagrange *et al* (1966) have not given any assignment of the strong polarised Raman line at 735 cm^{-1}. It is believed to originate in a vibration similar to mode *r* (Randle & Whiffen 1955) in which both the substituents move with the carbon atoms. The trigonal *p* mode (Randle and Whiffen 1955) evidently, gives rise to the very strong polarised Raman line at 1000 cm^{-1}. It may be noted that this line has been assigned by Garrigou-Lagrange *et al*, (1966) to mode 1 of benzene.

The weak Raman line at 850 cm^{-1} and the strong infrared band at 818 cm^{-1} are assigned to the modes 5 and 18*B* of benzene, respectively. The strong infrared band at 928 cm^{-1} is believed to arise from mode 17*B* of benzene while mode 17*A* of benzene gives rise to the weak Raman line at 956 cm^{-1}.

In the spectra of meta-cresol there are two vibration frequencies at 1246 cm^{-1} and 1280 cm^{-1} of which the former is observed as a strong absorption band in the

infrared spectrum of the pure liquid while the latter is found to appear both as a weak polarised Raman line and a strong infrared band of about the same frequency Garrigou-Lagrange *et al.* (1966) did not observe the band 1246 cm^{-1} while the band 1281 cm^{-1} has been assigned by them to mode e'' of Kohlrausch. Though the two frequencies in question appear to correspond to the frequencies 1210 and 1253 cm^{-1} of para-cresol, it is doubtful whether they originate in similar modes of vibration in the two molecules, because the modes e and e' of Kohlrausch cannot possibly occur in the case of meta-cresol.

Following the mode of assignments in the case of meta-disubstituted benzenes by Bogomolov (1962) the frequency 1281 cm^{-1} is assigned to vibration 13 in which there is symmetric in-phase stretching of C-CH_3 and C-OH bonds while the other frequency 1246 cm^{-1} may be attributed to vibration 7*B* where such stretching of the two bonds takes place in opposite phases.

It can be seen from table 2 that there are two strong absorption bands at 1495 and 1514 cm^{-1} in the infrared spectra of meta-cresol in the liquid state and and its solution in chloroform Garrigou-Lagrange *et al* (1966) who also studied the infrared absorption spectra of solutions of meta-cresol, observed a number of bands between 1460-1520 cm^{-1} and assigned the bands 1460 and 1490 cm^{-1}, to modes 19*A* and 19*B* respectively, of benzene. As these two bands have not been observed in the present investigation either in the spectra of the pure liquid or of its solutions, this assignment does not seem satisfactory and therefore, the bands 1495 and 1514 cm^{-1} have been assigned to modes 19*A* and 19*B*, respectively.

The assignment of the vibrational modes of the methyl group and some of the modes involving stretching of the CH bonds of the ring is also shown in table 2.

c) *Ortho-cresol*

The assignment of the vibration frequencies of ortho-cresol in the region 650-1650 cm^{-1} made by Brigodiot & Lebas (1965) is given in table 3. Excepting a few, most of the assignments have not been changed in the present investigation. However, none of the Raman frequencies below 700-cm^{-1} has been assigned by the above authors, though Mecke-Kerkhof (1951) have given assignment for some of these lines. According to Mecke-Kerkhof the moderately strong depolarised Raman line 529 cm^{-1} arises from mode 6*B* of benzene while mode 6*A* of benzene gives rise to the medium intensity polarised Raman line at 585 cm^{-1}. This is indicated in the table. Mercke-Kerkhof (1951) also assigned two vibrational frequencies in the range 200-450 cm^{-1} observed in the case of many other ortho-substituted benzenes, to two modes of vibration involving in-plane deformations of the bonds connecting the substituents to the ring. In the case of ortho-cresol the Raman line 275 cm^{-1} probably corresponds to one of these modes. This frequency has been assigned to mode 18*A* of benzene.

Kovner & Bogomolov (1959) have calculated all the vibrational frequencies of ortho-xylene and calculations for the out of plane vibrations of ortho-xylene and some other ortho-disubstituted benzenes are given by Nonnenmacher & Mecke (1961). Following these calculations, the depolarised Raman line 189 cm^{-1} assigned to modes $10B$ of benzene and the weak Raman line 442 cm^{-1} is assigned to mode $16B$ of benzene Assignements of other weak Raman lines have not been attempted.

The strong and polarised Raman line 749 cm^{-1} and the strong infrared absorption band 710 cm^{-1} are assigned to the modes 1 and 12 of benzene. Following the calculations of Kovner & Bogomolov (1959) and those of Nonnenmacher & Mecke (1961) the strong infrared band 750 cm^{-1} is assigned to mode 11, while the depolarised Raman line 847 cm^{-1} corresponding to the strong infrared band 842 cm^{-1} is assigned to mode 5 These are shown in table 3.

The Raman spectrum of ortho-cresol in the liquid state show two polarised Raman lines of medium intensity at 1237 and 1255 cm^{-1} The infrared spectrum of the liquid shows two strong bands at 1242 and 1255 cm^{-1} corresponding to the two Raman lines and a third strong band at 1208 cm^{-1} All these bands are also observed in the infrared spectra of ortho-cresol solutions. Brigodiot & Lebas (1965) who did not observe the infrared band 1242 cm^{-1} assigned the bands 1208 cm^{-1} and 1255 cm^{-1} to modes e and e' of Kohlrausch For reasons already stated in the case of meta-cresols, the author suggests that the two vibration frequencies be assigned to modes $20B$ and $7B$ of benzene It is believed that the band 1208 cm^{-1} which may correspond to the frequency 1205 cm^{-1} of para-cresol arises from an in-plane OH deformation mode

Some other minor changes made in the assignment given by Brigodiot & Lebas (1965) are indicated in table 3 The assignments of the vibrational frequencies of the methyl group and some of CH stretching vibrations of the ring are given in the same table.

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TABLE 1 Para-cresol

Raman Shift (Δ cm^{-1})	Infrared bands (ν cm^{-1})				Assignment	
Pure liquid	Pure liquid	Solution in CCl_4	Pure liquid	Solution	Garrigou-Lagrange *et al.* (1958)	Present work
	Present authors		Garrigou-Lagrange *et al.* (1958)			
*282 (0*b*) 338 (3*b*) *D* *406 (0) 465 (2) *P* 510 (1) 644 (5) *D*						16*B*/18*B* 10*B*/9*B* 16*A* 6*A* 11 6*B*
701 (1)	702 *m*	700 *w*	703	702	4	4
741 (1)	738 *s*		739	738 749		5
*809 (0)				804		10*A*
	814 *vs*	816 *s*		817	11/17*B*	17*B*
824 (3) *P*		826 *s*			10*A*	12 (*r'*)
844 (6) *P*	842 *s*	840 *s* 929 *w*	843	843 922 949	*d* 5	1(*r*)
969 (0)				985		17*A* 17*A*/5
1018 (0)	1018 *w*		1017	1016	18*A*	18*A*
1039 (0)	1040 *w* 1104 *s*	1105 *w*	1043 1105	1046 1101	substituent	substituent
**1118 ($\frac{1}{2}$)		1110 *w*	1115	1112	15	15
1170 (2) *P*	1172 *s*	1177 *s*	1172	1170	9*A*	9*A*
*1205 (2)				1205	substituent	δ(OH)
1216 (4) *P*				1212	*e*	*q* (Randle
	1235 *sb*		1235			& Whiffen,
1255 (2) *P*		1258 *s*		1254 1284	*'e*	*q'* 1955)
1297 (1)	1292*w* 1340 *msh*	1346 *w*	1306 1343	1292 1338	3	3
	1360 *sb*	1360 *mb*	1364	1368		14
1381 (4) *P*	1375 *msh* 1444 m	1436 *w*		1382 1430	substituent 14	δ_s (CH_3) δ_a (CH_3)
1460 (0) *D*		1468	1460	1468	19*B*	19*A*
1517 (0*b*)	1514 *vs*	1516 *vs*		1515 1572	19*A*	19*B*
1596 (2) *D*	1600 *m*	1602 *msh*		1598	8*B*	8*B*
1614 (4) *D*	1614 *m*	1618 *ms*		1618	8*A*	8*A*
+2889 (3) *P*						ν_s(CH_3)
2920 (4) *P*						ν_a(CH_3)
3014 (2) *P* 3037 (2) *P* 3060 (6) *P*						ν(CH)

*Data from Biswas (1955)

**Data from Garrigou-Lagrange *et al.* (1958)

+Observed in the present investigation.

TABLE 2 Meta-cresol

Raman shift ($\Delta\nu$ cm^{-1})	Infrared bands (ν cm^{-1})				Assignment
Pure Liquid	Pure liquid Present Authors	$CHCl_3$	Pure liquid Garrigou-Lagrange *et al.* (1966)	Garrigou-Lagrange *et al.* (1966)	Present work
214 (3b)*D*					11
241 (4b)*D*					10*A*
304 (2)*D*			307		9*A*
			442	16*B*	16*B*
518 (3)*P*			517	ν_c	6*A*
541 (2)*P*			537	ν_c	6*B*
565 (1)*D*			560		15
	688 *s*	688 *s*	686	4	4
735 (6)*P*	740 *mb*		734		*r* (Randle & Whiffen, 1955)
	756 *s*				
			768		
778 (0)	776 *vs*		776	11	10*B*
	181 *s*	820 *vs*			18*B*
850 (0)	844 *m*	846 *s*	842		5
			854	17*B*	
	880 *w*	882 *w*	872		
			925	17*A*	
	928 *s*	930 *s*	928		17*B*
+956			959		17*A*
1000 (10)*P*	1000 *w*	1004 *m*	1000	1	*p* (Randle & Whiffen, 1955)
+1039 (0)	1042	1043 *m*	1039	substituent	substituent
			1080	18*B*	
1085 (2)*P*	1086 *w*	1086 *wb*	1086	18*A*	18*A*
	1106 *m*	1108 *s*			substituent?
			1154		
1161 (4b)*D*	1160 *vs*	1160 *vsb*	1164	9*B*	9*B*
			1178		
			1186	δ(OH) *free*	
			1286	δ(OH) *assoc.*	
	1246 *vs*		1267	3	7*B*
1280 (2)*P*	1280 *vs*	1286 *vs*	1281		13
			1305		
		1314 *m*	1309	14	
	1345 *sb*	1334 *s*			14
1381 (4)*P*	1385 *w*	1386 *msh*	1377	δ_s (CH_3)	δ_s (CH_3)
			1403		
1441 (0)	1440 *m*	1444 *ssh*	1436	δ_a (CH_3)	δ_a (CH_3)
			1460	19*A*	
		1470 *sb*	1470		
			1490	19*B*	
	1495 *s*	1498 *s*	1500		19*A*
	1514 *vs*	1516 *vs*			19*B*
			1520		
			1538		
			1590	8*A*	
1592 (2)*D*	1594 *vs*	1600 *vs*			8*A*
			1596		
1615 (6)*D*	1615 *ssh*		1613		8*B*
		1620 *ssh*	1619		
++2871 (3)*P*					ν_s (CH_3)
2922 (4)*P*					ν_a (CH_3)
3050 (2)*P*? ++3061 (7b)*P*					ν (CH)

+ Data from Biswas (1955). ++Observed in the present [illegible]

TABLE 3 Ortho-cresol

Raman shift ($\Delta\nu$ cm^{-1})	Infrared bands (ν cm^{-1})			Assignment	
Pure Liquid	Pure liquid Present authors	Solution in CCl_4	Pure liquid Brigodiot & Lebas (1965)	Brigodiot & Lebas (1965)	Present work
189 (4b) *D*					10*B*
275 (3) *D*					18*A*
311 (0)					
442 (0)					16 *B*
529 (4) *D*					6*B*
585 (5) *P*					6*A*
* 646 (0)					
* 695 (0)			688		4
* 711 (0)	710 *s*	710 *s*	709 (50)	4	12
749 (10) *P*	750 *vs*		748 (397) 810		1, 11
847 (1) *D*	842 *vs*	842 *vs*	842 (75) 922 (11)	10 *B*	5
	928 *m*	930 *w*	926 (11)	17 *B*	17 *B*
986 (2b)	984 *m*	980 *wb*	984 (14) 1017	5	17 *A*
1044 (6) *P*	1044 *s*	1040 *msh*	1038 (34) 1043 (30)	18 *B* substituent	18*B*
*1094 (1)					
1107 (1)	1108 *vs*	1104 *s*	1102 (130)	9*B*	substituent ?
1150 (4b) *D*	1156 *ssh*	1153 *msh*	1149 *sh*		9 *B*
	1170 *vs*	1168 *vs*	1164 (115)	9*A*/15	
	1208 *vsb*	1210 *vs*	1205 (118) 1216 (64)	*e*	δ(OH)
1237 (4b) *P*	1242 *vsb*	1244 *vssh*			7*B*
1255 (3b) *P*	1255 *vs*	1256 *vs*	1254 (119)	*e'*	20*B*
	1300 *m*	1300 *m*	1299 (29)	14/3	3
	1330 *s*	1329 *s*	1324 (90)		
	1350 *msh*	1350 *w*			14
1381 (3) *D*	1388 *w*	1384 *w*	1380 (18)		$\delta_s(CH_3)$
1440 (1) *D*	1450 *msh*		1443 (33)	substituent	$\delta_a(CH_3)$
*1471 (1)	1466 *s*	1467 *s*	1462 (72)	substituent/19*A*	19*A*
**1484 (0b)	1496 *vs*	1495 *s*	1492 (85)	19*B*	19*B*
	1505 *ssh*		1508 (66)		2 × 750
1510 (1)	1515 *ssh*	1515 *msh*			
1592 (4) *D*	1592 *vs*	1593 *s*	1587 (65)	8*A*	8*A*
1615 (7) *D*	1610 *msh*	1612 *msh*	1608 (23)	8*B*	8*B*
**2865 (2) *P*					$\nu_s(CH_3)$
2920 (3b) *P*					$\nu_a(CH_3)$
3054 (6b) *P* 3073 (3b)					ν(CH)

*Data taken from Biswas (1955).

**Observed in the present investigation.

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